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IMMOBILIZATION OF TECHNETIUM AND NITRATE IN CEMENT-BASED MATERIALS

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ABSTRACT

The leachabilities of technetium and nitrate wastes immobilized in cement-based materials (i.e., grouts) have been investigated using ANS 16.1 test procedures. Factors found to affect the leachabilities include (1) grout mix ratio, (2) grout fluid density, (3) dry solid blend composition (including ground blast furnace slag), and (4) waste concentration.

INTRODUCTION

The presence of technetium in low-level radioactive waste is of increasing concern because of the potential biological hazard of the ^{99}Tc isotope. The method most frequently used to immobilize low-level radioactive waste involves the use of cement or cement-like materials which are chemically basic. The following reaction

$$TcO_2 + 4OH^- \rightarrow TcO_4^- + 2H_2O + 3e^-, \qquad (1)$$

which is thermodynamically spontaneous, indicates that technetium in the long term can be expected to be present as the pertechnetate ion in such media. A need to investigate technetium leaching properties from grout was recognized since the pertechnetate ion is a highly soluble species and since the grout (cement-based materials) method is known as an excellent method for immobilizing waste.

The authors have previously detailed various aspects of waste immobilization [1-5]. Historically, a moderate amount of research and development has been required to retrofit the grout method to a given waste. The purpose of the investigation reported here was to retrofit the method to the Double Shell Slurry Feed (DSSF) waste of the Westinghouse Hanford Operations facility. This investigation with the DSSF waste deals with the leaching properties of technetium and nitrate from a number of different grouts. Nitrate is important because it ordinarily has high solubilities and correspondingly high leach rates. Ground blast furnace slag, used as a cementing material in this investigation, had not been used before in investigations at Oak Ridge National Laboratory (ORNL); but it had previously been determined to be effective for immobilizing technetium by investigators at Savannah River Laboratories [6].

EXPERIMENTAL METHOD

Waste Composition

The waste used in this investigation was simulated Double Shell Slurry Feed (DSSF) from Westinghouse Hanford Operations, and its composition is shown in Table I. Major constituents include 8.73 M NaOH, 1.5 M $Al(NO_3)_3$, 0.44 M KOH, and 0.3 M Na_2CO_3. Most of the grouts that were investigated were prepared using a 50% dilution of the waste with water. A few grouts were prepared using a 33% dilution, i.e., 2 parts of waste with 1 part of water, and one series of tests was conducted with undiluted waste. The waste, or diluted forms of the waste, were mixed with dry solid blends as described in the following section. Technetium (^{99}Tc) tracer was added at the time of mixing as ammonium pertechnetate (NH_4TcO_4).

Table I. Chemical Constituents In Synthetic DSSF

Constituent	Concentration ($\underline{M}$)
NaOH	8.73
$Al(NO_3)_3$	1.50
KOH	0.44
Na_2CO_3	0.30
NaCl	0.20
PO_4^{3-}	0.12
SO_4^{2-}	0.10
$Mn(NO_3)_2$	0.10

18 Other Inorganic and Organic Constituents

Dry Solid Blends

The compositions of eleven dry blends that were mixed with the waste to prepare grouts for the leach tests are shown in Table II. The blends contained from 38 to 100 wt % ground blast furnace slag; from 0 to 43.2 wt % Type I-II Portland cement; from 0 to 47.5 wt % ASTM class F fly ash (from Centralia, WA); from 0 to 5 wt % lime; and from 0 to 7 wt % Indian Red pottery clay (IRPC). Reasons for use of these materials have been adequately discussed in other reports [4-6].

Typical chemical analyses of the slag, fly ash, and cement are shown in Table III. The ground blast furnace slag was obtained from Ash Grove Cement West, Inc. of Durkee, Oregon. The dry blends except for Blend 14 (100 wt % slag) were tumbled in a V-blender for 23 h before use.

Mixing and Curing Procedure

The mixing procedure consisted of adding the blended solids to the waste in a Model N-50 Hobart mixer for 30 s at a low stirring rate, ~139 rpm, and

Table II. Blend Compositions for DSSF Waste (wt %)

Blend No.	Ground Blast Furnace Slag	Type I-II Cement	Class F Fly Ash	Lime $Ca(OH)_2$	IRPC
3	70	25	-	-	5
6	49.8	43.2	-	-	7
9	75	20	-	-	5
14	100	-	-	-	-
15	90	10	-	-	-
17	95	-	-	5	-
18	88	-	-	5	7
19	47.5	-	47.5	5	-
20	47.5	-	40.5	5	7
21	38	10	47	5	-
22	38	10	40	5	7

Table III. Typical Blend Component Chemical Analyses (wt %)

	Ground Blast Furnace Slag	Class F Fly Ash	Type I-II Portland Cement
SiO_2	31.8	45.0	20.7
Al_2O_3	15.1	22.3	4.8
CaO	41.0	11.1	64.3
SO_3	2.0	0.1	2.8
Na_2O	0.1	4.8	0.1
K_2O	0.2	3.8	0.1
Fe_2O_3	0.7	5.5	2.5
MgO	7.3	2.0	3.8

then increasing the stirring rate to ~285 rpm (medium speed setting on the mixer) for 30 s. The specimens for the leach test were prepared by pouring freshly prepared grouts into cylindrical teflon molds (2.55 cm-diam by 4.80 cm-long) and allowing the grouts to stand or cure at 60°C in a humidity over at 100% humidity for 28 d.

Leaching Procedure

The cured grout specimens were then leached following the ANS-16.1 leaching procedure [7]. In that procedure, each grout specimen, after rinse off, was suspended in a 451 mL volume of water for 2 h and then moved to another 451 mL volume of water for 5 h and then similarly to other 451 mL volumes of water for 17, 24, 24, 24, 24, 336, 672, and 1032 h intervals to give a total leach time of 90 d. Three specimens were prepared and leached from each grout mix.

The leach solutions were each analyzed for ^{99}Tc and nitrate. The ^{99}Tc beta count was determined using a LKB model 1211 Rackbeta liquid scintillation counter. The nitrate concentration was determined using an Orion ion selective electrode with a pH/ISE meter.

Leachability Index Calculation

The effective diffusivity was calculated for each leach specimen (where less than 20% of the leachable species was leached) from the following expression:

$$D = \pi \left(\frac{a_n/A_o}{(\Delta t)_n}\right)^2 \left(\frac{V}{S}\right)^2 (T) \qquad (2)$$

where:

a_n = activity of a nuclide released from the specimen during leaching interval n, corrected for radioactive decay,

A_o = total activity of a given radionuclide in the specimen at the beginning of the leach test (i.e., after the initial 30-s rinse);

$(\Delta t)_n$ = $t_n - t_{n-1}$, duration of the n-th leaching interval, s.

D = effective diffusivity, cm^2/s,

V = volume of specimen, cm^3,

S = geometric surface area of the specimen as calculated from measured dimensions, cm^2, and

T = $[0.5\,(t_n^{0.5} + t_{n-1}^{0.5})]^2$, leaching time, representing the "mean time" of the leaching interval, s.

For leachates where more than 20% of the leaching species had leached from the specimen a slightly more complicated method involving the use of tables presented in the ANS-16.1 procedure [7] was used to calculate the effective diffusivity, D.

The calculated values of D were subsequently used to calculate leachability index [L_i] values using the following expression:

$$L_i = (0.1) \sum_{n=1}^{10} [\log (ß/D_i)]_n \quad (3)$$

where ß is a defined constant (1 cm^2/s) and D_i is the effective diffusivity of nuclide i calculated from the test data. It should be noted from Eq. (3) that values of L_i become greater as the diffusion rate D_i values become smaller. For purposes of this study, large values of L_i are desirable, and since L_i is a logarithm term, small increases in the values may be significant.

EXPERIMENTAL RESULTS

Typical leach rate results are shown in Fig. 1 for technetium and in Fig. 2 for nitrate. The plots in the figures are of normalized cumulative leached fraction vs the square root of time in hours. The normalized cumulative leached fraction is the $(a_n/A_o)(V/S)$ term from Eq. (2). As can be seen in Fig. 1, the early part of the technetium leach curves are non-linear up to ~5 d ($\sqrt{120}$ h). This non-linearity is considered to be a surface-related or wash-off problem and not indicative of the long term leach properties of the technetium in the grout specimens. Thus, values for what has been termed "post-wash-off leachability index" have been calculated for each technetium leach series. This term is the average leachability index for the specimens beginning with the 5th day and going out as far as the 90th day. The data in the figures are for 50 vol % dilutions of DSSF, as are all the ensuing ones, unless otherwise designated.

The effect of the grout mix ratio (the weight of dry solids blend mixed with a given volume of waste) on the leachability index for nitrate and technetium, L_i, can be seen for Blends 3, 14, and 19 in Fig. 3. There is a significant increase in the L_i for nitrate for Blend 19 as the mix ratio is increased from 960 to 1020 kg/m^3. For the other two blends, the nitrate L_i remains relatively constant. The post wash off L_i values for technetium increased for all three blends with increase in mix ratio, particularly for Blends 14 and 19, for the mix ratio increase from 960 to 1020 kg/m^3. It is also of interest that for a number of the blends, the technetium post-wash-off L_i values tended to increase with increase in grout fluid density, as can be seen in Fig. 4. Numerals beside the data points in the figure are blend numbers. The grout fluid density is the density of the grout immediately after it is mixed.

The effect of ground blast furnace slag content of the blends on technetium post-wash-off L_i can be seen in Fig. 5. Again, the numerals beside the data points in the figure are blend numbers. The L_i values for ^{99}Tc increase with increase in blend slag content as can be seen, with the largest increase occurring between 95 and 100 wt % slag, for the 960 kg/m^3 mix ratio. The L_i values for nitrate (not shown in the plot) also increased although less dramatically. The increases were from 7.5 to 8.2 and from 7.7 to 8.5, respectively, for the 960 and 1020 kg/m^3 mix ratio specimens, for slag increases from 70 to 100 wt %.

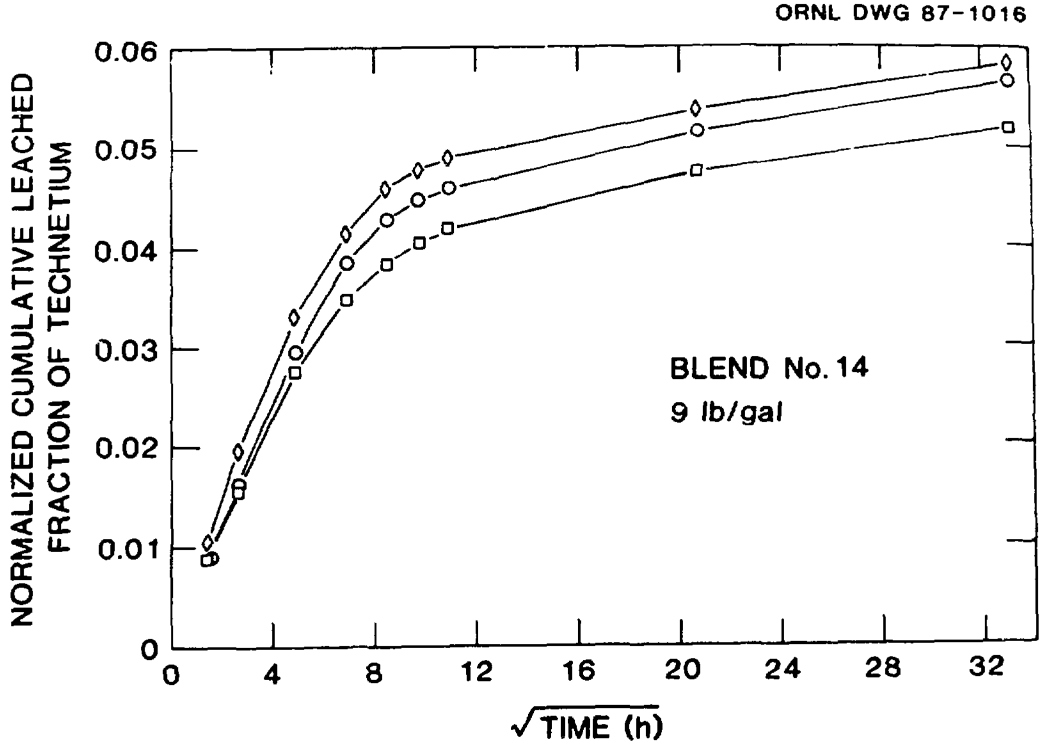

Fig. 1. Normalized cumulative leached fraction of technetium vs. th
root of time.

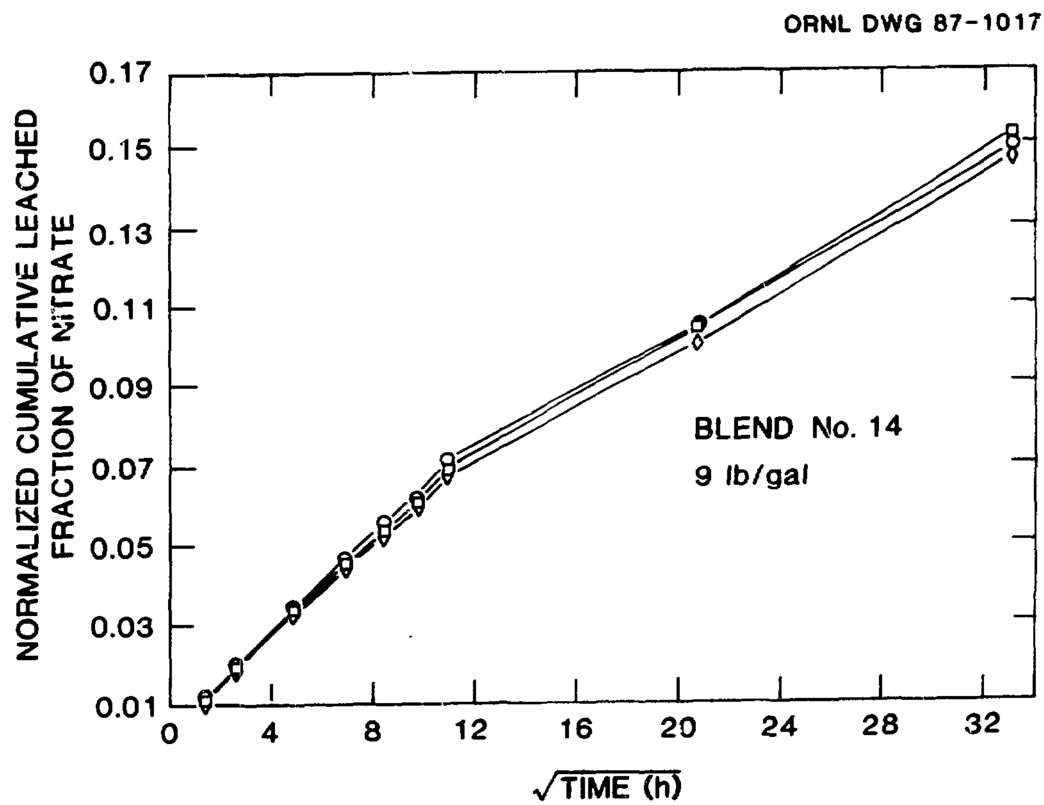

Fig. 2. Normalized cumulative leached fraction of nitrate vs. the squ
root of time.

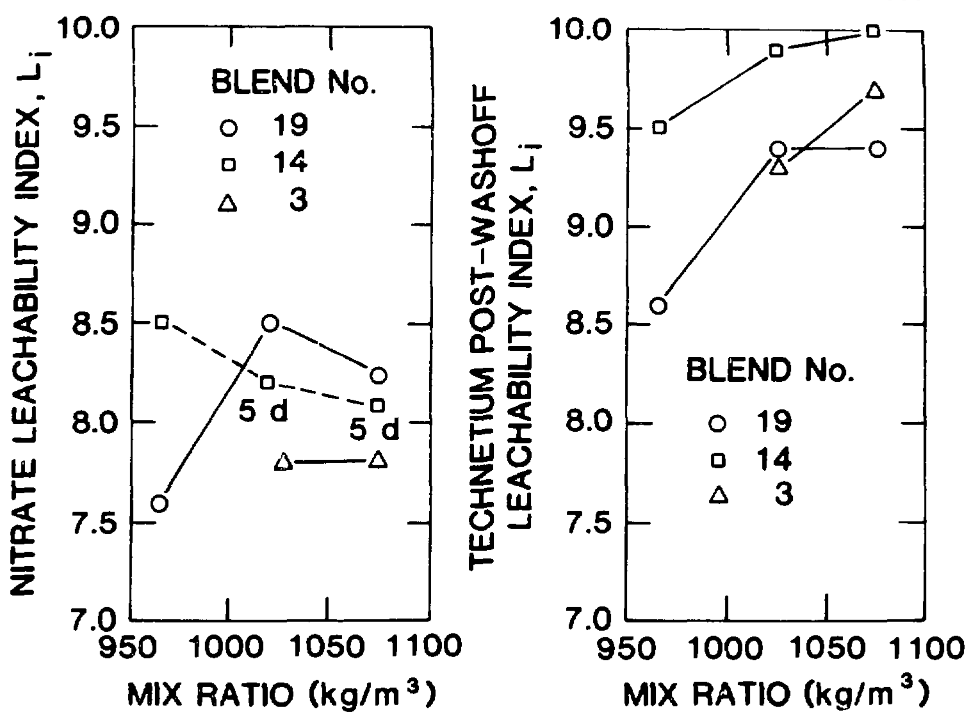

Fig. 3. Effect of grout mix ratio on nitrate and technetium post-was leachability indexes.

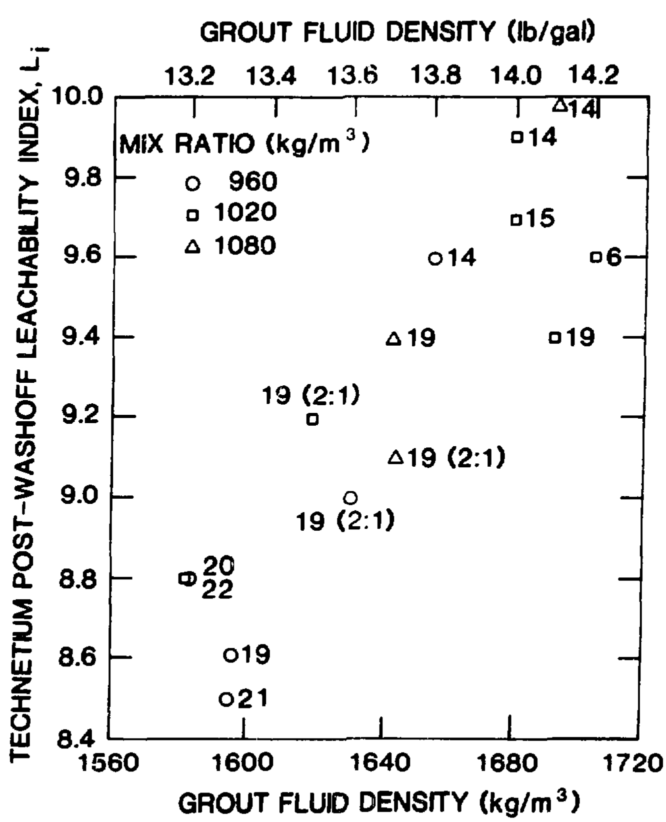

Fig. 4. Effect of grout fluid density on technetium post-wash-off leachability index.

The inclusion of 10 wt % Type I-II Portland cement and/or 7 wt % IRPC in blends where the major components were ground blast furnace slag and ASTM class F fly ash (Blends 19, 20, 21, 22), had only slight effects on nitrate and technetium leachability indexes of specimens prepared from 50 vol % dilutions of DSSF, as can be seen in Fig. 6. The indexes remained constant or decreased slightly with inclusion of the cement and clay.

Decreasing the waste (DSSF) concentration (by dilution with water) from 100% to 67% and from 67% to 50%, dramatically increased technetium post-drain-off L_i, as can be seen in Fig. 7 for specimens prepared using Blend 3. The index values ranged from a low of 7.4 for 840 kg/m^3 mix ratio specimens at 100% waste concentration, up to 9.8 for 1080 kg/m^3 mix ratio specimens with 50% waste concentration. Nitrate indexes appear to have been little effected by the waste concentration variation.

DISCUSSION

The ANS-16.1 procedure [7] calls for leachability indexes ≥7.0 for most radioactive isotopes (or other materials). Both ^{99}Tc and nitrate index values for most grouts tested in this work exceeded the 7.0 requirement. There are a number of literature references [8-10] showing that blended cements containing ground blast furnace slag and/or fly ash, form products with finer pore structures than are formed with ordinary cements, and that diffusion through these products is at a slower rate. Our results, showing greater leachability index values with increase in grout ground blast furnace slag content, increase in grout mix ratio, and increase in grout density are consistent with the literature information, to the extent that such blend modifications decrease pore size or otherwise favorably affect grout pore properties. The slag apparently has an additional affect in increasing ^{99}Tc leachability index values, which does not apply to the nitrate, since decreasing the waste concentration (or increasing the slag-to-waste concentration ratio) increases the ^{98}Tc but not the nitrate leachability index values. This affect is thought to result from the chemical reducing properties of the slag, which reduces the technetium from the pertectnetate to the dioxide, a less soluble and slower leaching species.

SUMMARY

Blends 14 (100 wt % slag) and 19 (47.5 wt % slag, 47.5 wt % ASTM class F fly ash, and 5 wt % lime) gave the best overall results. Technetium post-wash-off leachability indexes were >9.0 for 840, 1020, and 1080 kg/m^3 mix ratios for Blend 14; and ranged from 8.6 to 9.4 for Blend 19 for the same mix ratios. The nitrate leachability indexes for the two blends ranged from 7.6 to 8.5 depending on mix ratio.

In general, technetium post-wash-off leachability indexes increased with (1) increase in mix ratio, (2) grout fluid density, (3) blend ground blast furnace slag content, and (4) with decrease in the DSSF waste concentration.

Nitrate behaved very similarly to technetium in most tests, except that lower leachability indexes were obtained. In one major exception, dilution of the waste had little effect on the nitrate index values while greatly increasing the technetium post-drain-off index values.

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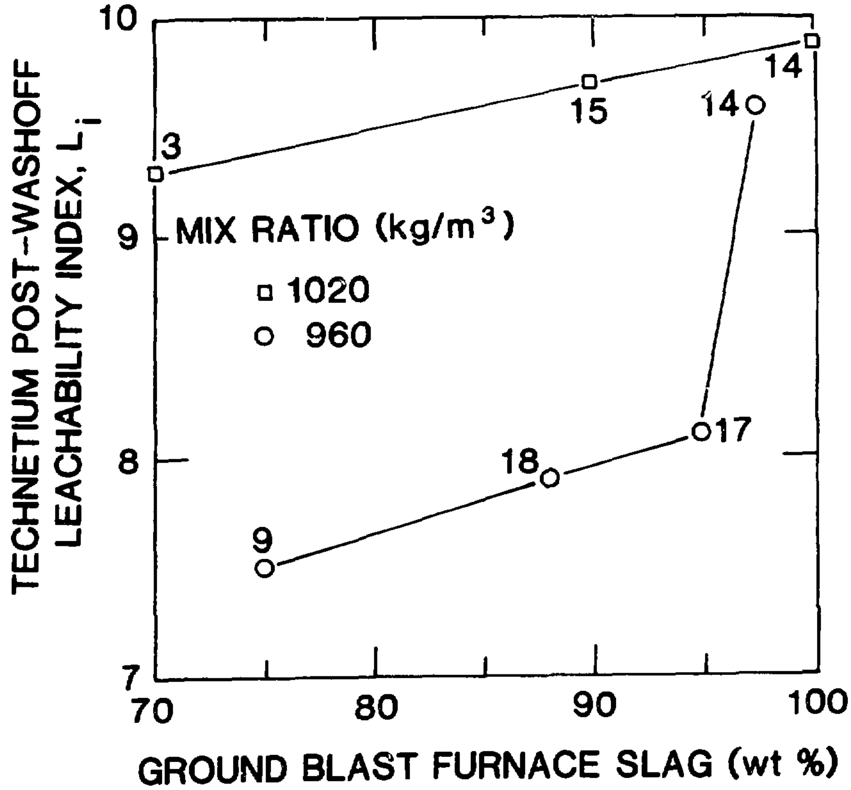

Fig. 5. Effect of blend ground blast furnace slag content on technetium post-wash-off leachability index.

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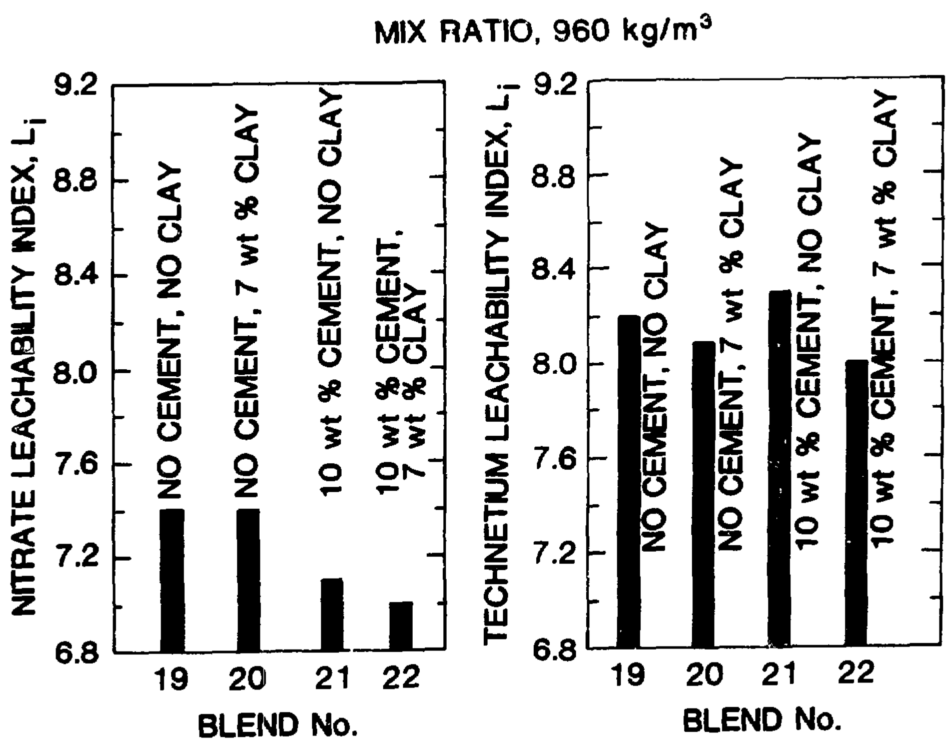

Fig. 6. Effect of Type I-II Portland cement and Indian Red Pottery clay on nitrate and technetium leachability index. Major dry-solid blend components were ground blast furnace slag and ASTM class F fly ash.

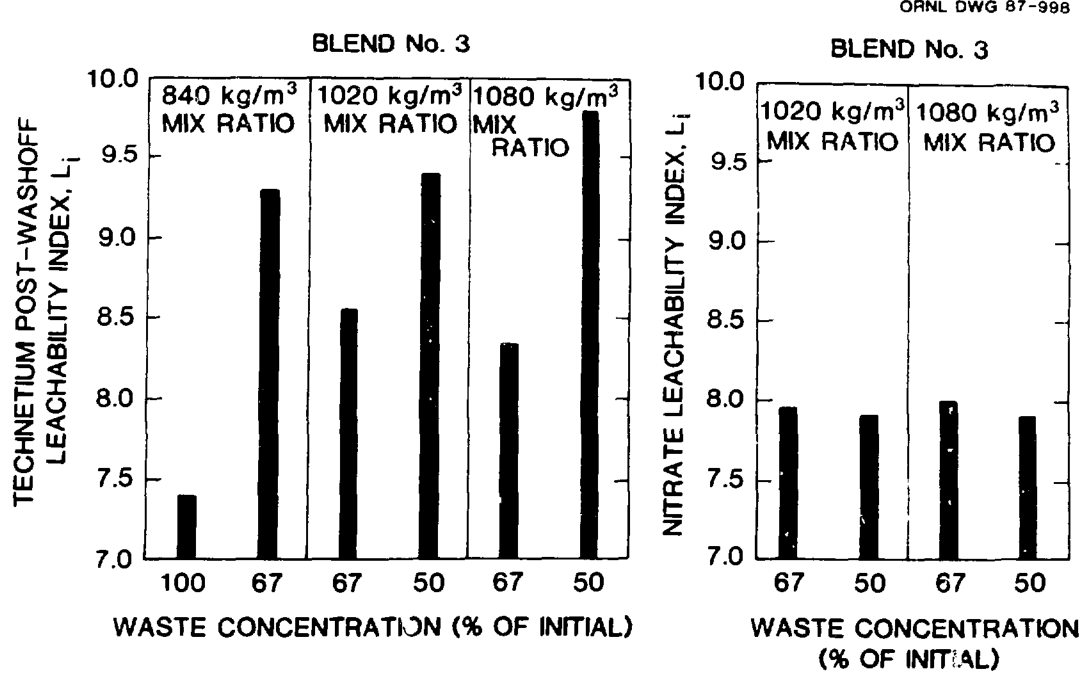

Fig. 7. Effect of waste concentration on technetium post-wash-off and nitrate leachability indexes for grouts formulated using Blend No. 3.

REFERENCES

1. O. K. Tallent, E. W. McDaniel, and T. T. Godsey, Fixation of Waste Materials in Grouts. Part II: An Empirical Equation for Estimating Compressive Strength For Grouts From Different Wastes, ORNL/TM-9680/PII (March 1986).

2. O. K. Tallent, E. W. McDaniel, R. D. Spence, and T. T. Godsey, Initial Formulation Results for Insitu Grouting of a Waste Trench at ORNL Site No. 6, ORNL/TM-10299(1987).

3. O. K. Tallent, T. L. Sams, T. Tamura, T. T. Godsey, C. L. Francis, and E. W. McDaniel, Grout Testing and Characterization for Shallow-Land Burial Trenches at the Idaho National Engineering Laboratory, ORNL/TM-9881 (1986).

4. O. K. Tallent, E. W. McDaniel and T. T. Godsey, Empirical Equation For Statistical Analysis of Waste Grout Data, Advances In Ceramics, 20, 297 (1987).

5. O. K. Tallent, E. W. McDaniel, K. E. Dodson, and T. T. Godsey, Empirical Correlations from Waste Grout Formulation Data, Nucl. Technol, 79, (1987).

6. C. A. Langton, Personal communication to O. K. Tallent, August 1987.

7. "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes," Prepared by the American Nuclear Society Standards Committee Working Group ANS-16.1. (June 20, 1984).

8. D. M. Roy and G. M. Idorn, "Hydration, Structure, and Properties of Blas Furnace Slag Cements, Mortars, and Concrete," ACI Journal/November-December 1982, p. 444.

9. Shiquin Li and Della M. Roy, "Investigation of Relations Between Porosity, Pore Structure, and Cl^- Diffusion of Fly Ash and Blended Cement Pastes," Cement and Concrete Research, 16, 749-759 (1986).

10. R. I. A. Kalik, D. M. Roy, M. W. Bornes, and C. A. Langton, "Slag Cement-Low Level Waste Forms at the Savannah River Plant," DP-MS-85-9, DE85 012328, (1985).